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The analog of Koopmans' theorem in spin-density functional theory

O. V. Gritsenko and E. J. Baerends^{a)}

Section Theoretical Chemistry, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

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For spin-unrestricted Kohn–Sham (KS) calculations on systems with an open shell ground state with total spin quantum number S , we offer the analog of the Koopmans'-type relation between orbital energies and ionization energies familiar from the Hartree–Fock model. When (case I) the lowest ion state has spin $S - 1/2$ (typically when the neutral molecule has a (less than) half filled open shell), the orbital energy of the highest occupied orbital (ϕ_H), belonging to the open shell with majority spin (α) electrons, is equal to the ionization energy to this lowest ion state with spin $S - 1/2$: $\epsilon_H^\alpha = -I^{S-1/2}(\phi_H^{-1})$. For lower (doubly occupied) orbitals the ionization ϕ_H^{-1} leaves an unpaired electron that can couple to the open shell to $S \pm 1/2$ states: $\epsilon_i^\beta \approx -I^{S+1/2}(\phi_i^{-1})$ (exact identity for $i = H - 1$), $\epsilon_i^\alpha \approx -\{[2S/(2S+1)]I^{S-1/2}(\phi_i^{-1}) + [1/(2S+1)]I^{S+1/2}(\phi_i^{-1})\}$, reducing to a simple average in the case of a doublet ground state (single electron outside closed shells). When the lowest ion state has spin $S + 1/2$ (case II; typically for more than half filled open shells): $\epsilon_H^\alpha = \epsilon_H^\beta = -I^{S+1/2}(\phi_H^{-1})$; for $i < H$, $\epsilon_i^\beta \approx -I^{S+1/2}(\phi_i^{-1})$, $\epsilon_i^\alpha \approx -\{[2S/(2S+1)]I^{S-1/2}(\phi_i^{-1}) + [1/(2S+1)]I^{S+1/2}(\phi_i^{-1})\}$. A physical basis is thus provided for the KS orbital energies also in the spin unrestricted case and an explanation is given for the common observation in approximate Kohn–Sham calculations of more negative majority spin (α) levels ϵ_i^α for $i < H$, than minority spin levels ϵ_i^β . © 2002 American Institute of Physics. [DOI: 10.1063/1.1516800]

I. INTRODUCTION

Spin-density functional theory (SDFT),^{1–3} an extended version of DFT, operates with the unequal (for open-shell systems) spin-densities ρ_σ and the potentials $\nu_{s\sigma}$ of the spin-unrestricted Kohn–Sham (KS) equations

$$\left\{ -\frac{1}{2}\nabla^2 + \nu_{s\sigma}(\mathbf{r}_1) \right\} \phi_{i\sigma}(\mathbf{r}_1) = \epsilon_{i\sigma} \phi_{i\sigma}(\mathbf{r}_1), \quad (1)$$

where $\phi_{i\sigma}$ are the KS spin-orbitals, $\rho_\sigma(\mathbf{r}_1) = \sum_i^N |\phi_{i\sigma}(\mathbf{r}_1)|^2$, and $\epsilon_{i\sigma}$ are their energies. In spite of many successful applications,^{4–6} the foundation and interpretation of SDFT remains a matter of discussion and concern. Recently, the nonuniqueness of $\nu_{s\sigma}$ was discussed and a critical reexamination of previous applications of SDFT was called for.⁷ This nonuniqueness manifests itself, for example, in arbitrariness in the (physically relevant) relative constant shifts of $\nu_{s\alpha}$ and $\nu_{s\beta}$.

In this paper key equations of SDFT are derived (with neglect of magnetic interactions) from the Schrödinger equation and the SDFT analog of the Koopmans' interpretation of the Hartree–Fock model⁸ is proposed. This is achieved with the expansion of N electron wave function in terms of $(N - 1)$ wave functions of a particular spin and the corresponding Dyson spin-orbitals and with the analysis in terms of the spin-resolved conditional probability amplitudes. Previously, similar spin-restricted techniques have been applied^{9–11} to provide the interpretation of DFT for closed-shell systems.

In Sec. II of this paper the Dyson-orbital expansion of the N electron wave function is introduced and the spin-resolved conditional probability amplitudes Φ_σ are defined. Exact equations for the square root of ρ_σ are derived by

means of incomplete integration and spin-projection of the Schrödinger equation. In Sec. III the same technique is applied to the KS noninteracting system. It is shown that, with proper individual gauges of $\nu_{s\sigma}$ to fix their nonuniqueness mentioned in Ref. 7, the key components of $\nu_{s\sigma}$, the spin-unrestricted exchange-correlation (xc) potentials $\nu_{xc,\sigma}$ can be represented in a physically meaningful way as the potentials $\nu_{xc,\sigma}^{\text{hole}}$ of the xc hole surrounding an electron with the spin σ plus corrections defined in terms of the spin-resolved conditional probability amplitudes. In Sec. IV exact relations between the KS spin-orbital energies $\epsilon_{i\sigma}$ and the potentials $\{I_i^S\}$ of ionization to $(N - 1)$ electron states of a certain spin S are obtained. Analysis of these equations provides the KS SDFT analog of Koopmans' theorem. In Sec. V the implication of the present results for SDFT are discussed and the conclusions are drawn.

II. EQUATION FOR THE SQUARE ROOT OF ρ_σ

We start with the expansion of a pure N electron ground state Ψ_0^{NSS} , the “top” component of the multiplet $\{\Psi^{NSM}\}$ of degenerate states with the spin S , in terms of pure $(N - 1)$ electron states $\Psi_i^{(N-1)S'M'}$ and the corresponding Dyson orbitals $d_{i\sigma}(\mathbf{r}_1)\sigma(s_1)$,

$$\begin{aligned} \Psi_0^{NSS}(\mathbf{x}_1, \dots, \mathbf{x}_N) &= \frac{1}{\sqrt{N}} \sum_{\sigma=\alpha,\beta} \sum_{S'=(S-m_\sigma)}^{S+1/2} \sum_{i[S'(S-m_\sigma)]} d_{i\sigma}(\mathbf{r}_1)\sigma(s_1) \\ &\quad \times \Psi_i^{(N-1)S'(S-m_\sigma)}(\mathbf{x}_2, \dots, \mathbf{x}_N), \\ d_{i\sigma}(\mathbf{r}_1)\sigma(s_1) &= \sqrt{N} \int \Psi_i^{(N-1)S'(S-m_\sigma)*}(\mathbf{x}_2, \dots, \mathbf{x}_N) \\ &\quad \times \Psi_0^{NSS}(\mathbf{x}_1, \dots, \mathbf{x}_N) d\mathbf{x}_2 \cdots d\mathbf{x}_N. \end{aligned} \quad (2)$$

^{a)}Electronic mail: baerends@chem.vu.nl

Throughout the paper for any wave function Ψ^{NSM} the first superscript index N is the number of electrons, the second one S is its spin, and the third one M is its eigenvalue for the operator \hat{S}_z . In Eq. (2) m_σ is the eigenvalue of \hat{S}_z for the functions $\sigma(s_1)$, $\hat{S}_z\sigma(s_1)=m_\sigma\sigma(s_1)$, $m_\alpha=+1/2$, $m_\beta=-1/2$, and the index $i[S'(S-m_\sigma)]$ under the last summation enumerates all $(N-1)$ electron states $\Psi_i^{(N-1)S'(S-m_\sigma)}$ with the spin S' and the eigenvalue $(S-m_\sigma)$ of \hat{S}_z as well as the corresponding Dyson spin-orbitals $d_{i\sigma}$. The Dyson orbitals are pure spin-orbitals when Ψ_0^N and the $\Psi_i^{(N-1)}$ are spin eigenfunctions. It is also possible to expand the wave function using the spin-resolved conditional probability amplitudes $\Phi_\sigma(\mathbf{x}_2\cdots\mathbf{x}_N|\mathbf{r}_1)=\Psi(\mathbf{r}_1\sigma,\mathbf{x}_2\cdots\mathbf{x}_N)/\sqrt{\rho_\sigma(\mathbf{r}_1)/N}$,

$$\Psi_0^{NSS}(\mathbf{x}_1,\dots,\mathbf{x}_N)=\sum_{\sigma=\alpha,\beta}\sqrt{\frac{\rho_\sigma(\mathbf{r}_1)}{N}}\times\Phi_\sigma(\mathbf{x}_2\cdots\mathbf{x}_N|\mathbf{r}_1)\sigma(s_1). \quad (3)$$

Φ_σ is an $(N-1)$ -electron wave function, the square of which is the probability to find electrons $2\cdots N$ with spatial and spin coordinates $\mathbf{x}_2=\mathbf{r}_2,s_2\cdots\mathbf{x}_N=\mathbf{r}_N,s_N$, if electron 1 is at the position \mathbf{r}_1 with spin σ .^{9,12} The one-electron density of $\Phi_\sigma(\mathbf{x}_2\cdots\mathbf{x}_N|\mathbf{r}_1)$ is the probability for electrons of both α and β spin to be at \mathbf{r}_2 when electron 1 is known to be at position $\mathbf{r}_1\sigma$, i.e., the conditional density $\rho^{\text{cond},\alpha+\beta|\sigma}(\mathbf{r}_2|\mathbf{r}_1)=(N-1)\int\Phi_\sigma(\mathbf{x}_2\cdots\mathbf{x}_N|\mathbf{r}_1)\Phi_\sigma^*(\mathbf{x}_2\cdots\mathbf{x}_N|\mathbf{r}_1)d\mathbf{x}_3\cdots d\mathbf{x}_N$. It describes the exchange and correlation holes in the total electron density surrounding a reference electron at \mathbf{r}_1 with spin σ : $\rho_{\text{xc},\sigma}^{\text{hole}}(\mathbf{r}_2|\mathbf{r}_1)=\rho^{\text{cond},\alpha+\beta|\sigma}(\mathbf{r}_2|\mathbf{r}_1)-\rho(\mathbf{r}_2)$ (cf. Ref. 13). It follows from Eqs. (2) and (3), that for the minor spin (β) only the states $\Psi_i^{(N-1)(S+1/2)(S+1/2)}$ with $S'=(S+1/2)$ ($M'=S+1/2$) contribute to Φ_β , while for the major spin (α) the states $\Psi_i^{(N-1)(S\pm 1/2)(S-1/2)}$ with $M'=S-1/2$ and both $S'=(S+1/2)$ and $S'=(S-1/2)$ contribute to Φ_α . For each spin the sum over all $d_{i\sigma}$ yields the spin-density $\rho_\sigma(\mathbf{r}_1)=\sum_i|d_{i\sigma}(\mathbf{r}_1)|^2$.

With the expansion (3), an effective one-electron equation can be obtained for the spin-density $\sqrt{\rho_\sigma}$ from the Schrödinger equation $\hat{H}^N\Psi_0^{NSS}=E_0^{NSS}\Psi_0^{NSS}$ by partitioning of its (spin-free) Hamiltonian \hat{H}^N into the $(N-1)$ electron Hamiltonian \hat{H}^{N-1} and the remainder,

$$\hat{H}^N=-\frac{1}{2}\nabla_1^2+\nu_{\text{ext}}(\mathbf{r}_1)+\sum_{j=2}^N\frac{1}{|\mathbf{r}_1-\mathbf{r}_j|}+\hat{H}^{N-1}.$$

For each spin σ we also subtract from both sides of the Schrödinger equation the term $E_0^{(N-1)(\sigma)}\Psi_0^{NSS}$, where $E_0^{(N-1)(\sigma)}$ is the lowest energy for the states $\Psi_i^{(N-1)S'(S-m_\sigma)}$, which contribute to Φ_σ . This is done in order to obtain asymptotic decay to zero for the effective potentials we will be considering (see the following). For $\sigma=\beta$ $E_0^{(N-1)(\sigma)}$ is the lowest energy of all ion states of spin $S+1/2$. For $\sigma=\alpha$ however it is the lowest energy of all ion states of either spin $S'=S+1/2$ or spin $S'=S-1/2$. Typically, if the system has a (less than) half filled open shell containing p electrons outside closed shells, the ground state will according to Hund's rule be a state with $S=p/2$, and the lowest ion state will correspond to ionization out of this open

shell, the state with maximum spin multiplicity $S'=(p-1)/2=S-1/2$ corresponding to the ground state of the ion. If the ground state has a more than half filled open shell, ionization will lead to a lowest ion state of higher spin multiplicity $S'=S+1/2$. We will denote these cases as I and II, respectively.

Inserting the expansion (3) and the partitioning of the Hamiltonian in the Schrödinger equation with $E_0^{(N-1)(\sigma)}\Psi_0^{NSS}$ subtracted, and then multiplying by the spin-amplitude $\Phi_\sigma(\mathbf{x}_2,\dots,\mathbf{x}_N|\mathbf{r}_1)\sigma(s_1)$ and integrating over $s_1,\mathbf{x}_2,\dots,\mathbf{x}_N$, we obtain an exact equation for the square root of ρ_σ ,

$$\left\{-\frac{1}{2}\nabla^2+\nu_{\text{ext}}(\mathbf{r}_1)+\nu_H(\mathbf{r}_1)+\nu_{\text{xc},\sigma}^{\text{hole}}(\mathbf{r}_1)+\nu_{\text{kin},\sigma}(\mathbf{r}_1)+\nu_\sigma^{N-1}(\mathbf{r}_1)\right\}\sqrt{\rho_\sigma(\mathbf{r}_1)}=\mu_\sigma\sqrt{\rho_\sigma(\mathbf{r}_1)}, \quad (4)$$

where $\mu_\sigma=E_0^{NS}-E_0^{(N-1)(\sigma)}$ is the lowest ionization energy to states contributing to Φ_σ , as defined previously (different for Φ_α and Φ_β in case I but the same in case II). This derivation is analogous to the one for the total density in the spin-restricted case.^{9,12,14} To derive Eq. (4), we use the normalization property of the spin-amplitude $\langle\Phi_\sigma|\Phi_\sigma\rangle=1$ at all \mathbf{r}_1 .

With Eq. (4) we express the potential of the Schrödinger equation for $\sqrt{\rho_\sigma}$ as a sum of physically meaningful potentials. Besides the standard external potential ν_{ext} and the Hartree potential of the electrostatic electron repulsion ν_H , these are the potential of the xc hole $\nu_{\text{xc},\sigma}^{\text{hole}}$ for electrons with the spin σ ,

$$\nu_{\text{xc},\sigma}^{\text{hole}}(\mathbf{r}_1)=\left\langle\Phi_\sigma\left|\sum_{j=2}^N\frac{1}{|\mathbf{r}_1-\mathbf{r}_j|}\right|\Phi_\sigma\right\rangle-\nu_H(\mathbf{r}_1)=\sum_{\sigma'}\int d\mathbf{r}_2\frac{\rho_\sigma(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}[g_{\sigma\sigma'}(\mathbf{r}_1,\mathbf{r}_2)-1] \quad (5)$$

($g_{\sigma\sigma'}$ is the pair-correlation function), the kinetic contribution $\nu_{\text{kin},\sigma}(\mathbf{r}_1)=\langle\Phi_\sigma|-\frac{1}{2}\nabla_1^2|\Phi_\sigma\rangle$, and the potential ν_σ^{N-1} ,

$$\begin{aligned}\nu_\sigma^{N-1}(\mathbf{r}_1)&=\langle\Phi_\sigma|\hat{H}^{N-1}|\Phi_\sigma\rangle-E_0^{(N-1)(\sigma)}\\&=\sum_{S'=(S-m_\sigma)}^{S+1/2}\sum_{i[S'(S-m_\sigma)]}\frac{|d_{i\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma(\mathbf{r}_1)}\\&\quad\times(E_i^{(N-1)S'}-E_0^{(N-1)(\sigma)}).\end{aligned} \quad (6)$$

The first term of ν_σ^{N-1} is the energy of $(N-1)$ electrons calculated under the condition that the reference electron with the spin σ is at \mathbf{r}_1 . Subtraction of the energy $E_0^{(N-1)(\sigma)}$ provides the natural gauge (zero at infinity) for ν_σ^{N-1} , which allows it to be expressed in the second line of Eq. (6) as the statistical average over the Dyson spin-orbitals of excitations $(E_i^{(N-1)S'}-E_0^{(N-1)(\sigma)})$ in the $(N-1)$ electron system. This also fixes the gauge of the total potential of Eq. (4) to zero at infinity, with which the eigenvalue μ_σ acquires the meaning of ionization potential. Note that μ_σ determines the asymptotic decay of the spin density, $\rho_\sigma\sim\exp(-2\sqrt{-2\mu_\sigma})$. In case I the densities ρ_α and ρ_β will decay

differently, but in case II, where $\mu_\alpha = \mu_\beta$, they must have similar asymptotic behavior, which fits in with the fact that a more than half filled shell requires the shell also to contain minority spin electrons.

III. EXPRESSION FOR THE SPIN-UNRESTRICTED KS XC POTENTIAL

With Eq. (4) the potential of the Schrödinger equation for $\sqrt{\rho_\sigma}$ is expressed through the potentials of the interacting electron system. Alternatively, one can express it in terms of the potentials of the noninteracting KS system with the same ground-state spin-densities ρ_σ as the interacting system considered previously. We are using the top component of the spin multiplet of the interacting system to ensure that the spin densities ρ_σ of the interacting wave function $\Psi^{NS(M=S)}$ can be represented with a single determinant ground state wave function $\Psi_{s,(M=S)}^N$ of the noninteracting system, the latter being an eigenfunction of the spin angular-momentum operator \hat{S}_z with the eigenvalue $M=S$. In particular, in the present case of Ψ_0^{NSS} we consider the determinant $\Psi_{s,(M=S)}^N$ with N_α α electrons and N_β β electrons, $S=(N_\alpha-N_\beta)/2$. The Hamiltonian \hat{H}_s^N of the Schrödinger equation for the noninteracting system $\hat{H}_s^N \Psi_{s,(M=S)}^N = E_{s,(M=S)}^N \Psi_{s,(M=S)}^N$ is just

$$\hat{H}_s^N = \sum_{j=1}^N -\frac{1}{2} \nabla_j^2 + \sum_{j=1}^N \sum_{\sigma} |\sigma(s_j)\rangle \nu_{s\sigma}(\mathbf{r}_j) \langle \sigma(s_j)|,$$

where $\nu_{s\sigma}(\mathbf{r}_j)$ are the KS potentials from Eq. (1), which we represent as the sum $\nu_{s\sigma} = \nu_{\text{ext}} + \nu_H + \nu_{\text{xc},\sigma}$, with $\nu_{\text{xc},\sigma}$ being the xc potential for electrons with the spin σ . Then, the total energy E_s^N is just the sum of the energies of the occupied orbitals

$$E_s^N = \sum_{\sigma=\alpha,\beta} \sum_i^{N_\sigma} \epsilon_{i\sigma}.$$

In analogy with the interacting case considered previously, we introduce the “noninteracting” spin-resolved conditional probability amplitude $\Phi_{s\sigma}(\mathbf{x}_2 \cdots \mathbf{x}_N | \mathbf{r}_1) = \Psi_s^N(\mathbf{r}_1, \mathbf{x}_2 \cdots \mathbf{x}_N) / \sqrt{\rho_\sigma(\mathbf{r}_1)/N}$, which due to the simple nature of the noninteracting wave function can be written as a finite sum over the occupied KS orbitals $\phi_{i\sigma}$ (which are the Dyson orbitals of this system) and the ion states $\Psi_{s,(S-m_\sigma),i}^{N-1}$ resulting from removal of this orbital from the determinant $\Psi_{s,(M=S)}^N$, $\Phi_{s\sigma}(\mathbf{x}_2 \cdots \mathbf{x}_N | \mathbf{r}_1) = [\rho_\sigma(\mathbf{r}_1)/N]^{-1/2} \times \sum_{i=1}^{N_\sigma} \psi_{i\sigma}(\mathbf{r}_1) \times \Psi_{s,(S-m_\sigma),i}^{(N-1)}(\mathbf{x}_2, \dots, \mathbf{x}_N)$. Then, one can apply to the noninteracting Schrödinger equation the same operations as those applied previously to the interacting one. We express the determinant $\Psi_{s,(M=S)}^N$ in terms of the spin-resolved conditional amplitudes $\Phi_{s\sigma}$, subtract for each spin σ the term $E_{s,0,(M=S)}^{N-1} \Psi_{s,0,(M=S)}^N$ (where $E_{s,0,(M=S)}^{N-1} = \sum_{i=1}^{N_\sigma-1} \epsilon_{i\sigma}$ + $\sum_{i=1}^{N_{\sigma'}} \epsilon_{i\sigma'}$ is the lowest energy of the ion states with $M=S-m_\sigma$) from both sides of the equation and then multiply the resulting equation by $\Phi_{s\sigma}(\mathbf{x}_2, \dots, \mathbf{x}_N | \mathbf{r}_1) \sigma(1)$ and integrate over $s_1, \mathbf{x}_2, \dots, \mathbf{x}_N$. With this, we obtain the following equation for ρ_σ :

$$\left\{ -\frac{1}{2} \nabla^2 + \nu_{\text{ext}}(\mathbf{r}_1) + \nu_H(\mathbf{r}_1) + \nu_{\text{xc},\sigma}(\mathbf{r}_1) + \nu_{s,\text{kin},\sigma}(\mathbf{r}_1) + \nu_{s\sigma}^{N-1}(\mathbf{r}_1) \right\} \sqrt{\rho_\sigma(\mathbf{r}_1)} = \mu_\sigma \sqrt{\rho_\sigma(\mathbf{r}_1)}, \quad (7)$$

where $\nu_{s,\text{kin},\sigma}$ is the noninteracting “kinetic” potential $\nu_{s,\text{kin},\sigma}(\mathbf{r}_1) = \langle \Phi_{s\sigma} | -\frac{1}{2} \nabla_1^2 | \Phi_{s\sigma} \rangle$ and the potential $\nu_{s\sigma}^{N-1}$ is

$$\nu_{s\sigma}^{N-1}(\mathbf{r}_1) = \langle \Phi_{s\sigma} | \hat{H}_s^{N-1} | \Phi_{s\sigma} \rangle - E_{s,0,(M=S-m_\sigma)}^{(N-1)} = \sum_i^{N_\sigma} \frac{|\phi_{i\sigma}(\mathbf{r}_1)|^2}{\rho_\sigma(\mathbf{r}_1)} (\epsilon_{N\sigma} - \epsilon_{i\sigma}). \quad (8)$$

The natural gauge $\nu_{s\sigma}^{N-1}(\mathbf{r}_1) \rightarrow 0$ (and hence the total $\nu_s(\mathbf{r}_1) \rightarrow 0$) at $|\mathbf{r}_1| \rightarrow \infty$ is provided by subtraction of $E_{s,0,(M=S-m_\sigma)}^{(N-1)}$. The only exception is the nodal surface of the highest occupied orbital $\phi_{N\sigma}$, a set of measure zero, on which $\nu_{s\sigma}^{N-1}(\mathbf{r}_1)$ according to Eq. (8) approaches asymptotically the positive constant $(\epsilon_{N\sigma} - \epsilon_{(N-1)\sigma})$. The nodal-surface structure of the KS potential has been considered in Ref. 15. Except for this set of measure zero, the asymptotic behavior of $\sqrt{\rho_\sigma}$ is determined by the eigenvalue $\mu_\sigma = E_{s,0,(M=S)}^N - E_{s,0,(M=S-m_\sigma)}^{(N-1)}$. Since the asymptotic behavior is also determined by the density of the highest occupied KS orbital, we must have $\mu_\sigma = \epsilon_{N\sigma}$. This shows that in case II, where $\mu_\alpha = \mu_\beta$ and the asymptotic decay of ρ_α and ρ_β is equal, the highest occupied orbital energies of α and β spin have to be equal, and are equal to the lowest ionization energy (to a state with $S'=S+1/2$), since also $\mu_\sigma = E_0^{NS} - E_0^{(N-1)(\sigma)}$, see Eq. (4). In case I, $E_0^{(N-1)(\alpha)} = E_0^{(N-1)(S-1/2)}$, the decay of ρ_α is governed by $\mu_\alpha = E_0^{NS} - E_0^{(N-1)(S-1/2)}$ and the highest occupied orbital energy of the α -spin orbitals is the ionization energy $-\mu_\alpha$ to the lowest ion state of spin $S'=S-1/2$. The decay of ρ_β is in case I governed by $\mu_\beta = E_0^{NS} - E_0^{(N-1)(S+1/2)}$ and the highest energy of the spin- β orbitals will be the ionization energy $-\mu_\beta$ to the lowest ion state of spin $S'=S+1/2$ (these results for case I were already obtained by Almladh and von Barth¹⁶). The difference in orbital energies for α and β orbitals in case I is understandable since in this case the highest occupied β spin KS orbital will not belong to the open shell but to a lower lying closed shell (in the KS system the shell structure of the interacting electron system usually also exists, at least approximately). The chosen gauge allows the potential $\nu_{s\sigma}^{N-1}$ to be expressed as the statistical average (8) over the occupied KS spin-orbitals $\phi_{i\sigma}$ of excitations in the $(N-1)$ electron noninteracting system, which are the differences $(\epsilon_{N\sigma} - \epsilon_{i\sigma})$ between the energies of the highest occupied molecular spin- σ orbital $\phi_{N\sigma}$ and the spin-orbital $\phi_{i\sigma}$.

Comparing Eqs. (4) and (7), we obtain for the spin-unrestricted xc potentials $\nu_{\text{xc}\sigma}$ the following expressions:

$$\nu_{\text{xc},\sigma}(\mathbf{r}_1) = \nu_{\text{xc},\sigma}^{\text{hole}}(\mathbf{r}_1) + [\nu_{\text{kin},\sigma}(\mathbf{r}_1) - \nu_{s,\text{kin},\sigma}(\mathbf{r}_1)] + [\nu_{s\sigma}^{N-1}(\mathbf{r}_1) - \nu_{s\sigma}^{N-1}(\mathbf{r}_1)]. \quad (9)$$

With Eq. (9), $\nu_{\text{xc}\sigma}$ is represented in a physically meaningful way as the potential $\nu_{\text{xc},\sigma}^{\text{hole}}$ of the xc hole surrounding an electron with the spin σ at \mathbf{r}_1 plus the correction $\nu_{c,\text{kin},\sigma} = \nu_{\text{kin},\sigma} - \nu_{s,\text{kin},\sigma}$ due to the correlation kinetic effect, plus

the correction $\nu_{\text{resp},\sigma} = \nu_{\sigma}^{N-1} - \nu_{s\sigma}^{N-1}$ to the energy of $(N-1)$ electrons due to the correlation with the reference electron at \mathbf{r}_1, σ . Note, that the last component of $\nu_{\text{xc}\sigma}$, the “response” potential $\nu_{\text{resp},\sigma}$, can be alternatively defined through the functional derivatives with respect to ρ_{σ} of the pair-correlation function $g_{\sigma\sigma'}$ and the correlation kinetic potential $\nu_{c,\text{kin},\sigma}$,^{10,17}

$$\begin{aligned} & \nu_{\sigma}^{N-1}(\mathbf{r}_1) - \nu_{s\sigma}^{N-1}(\mathbf{r}_1) \\ &= \nu_{\text{resp},\sigma}(\mathbf{r}_1) \\ &= \sum_{\sigma' \neq \sigma} \int d\mathbf{r}_2 d\mathbf{r}_3 \frac{\rho_{\sigma'}(\mathbf{r}_2) \rho_{\sigma''}(\mathbf{r}_2)}{|\mathbf{r}_2 - \mathbf{r}_3|} \frac{\delta g_{\sigma'\sigma''}(\mathbf{r}_2, \mathbf{r}_3)}{\delta \rho_{\sigma}(\mathbf{r}_1)} \\ &+ \sum_{\sigma'} \int d\mathbf{r}_2 \rho_{\sigma'}(\mathbf{r}_2) \frac{\delta \nu_{c,\text{kin},\sigma'}(\mathbf{r}_2)}{\delta \rho_{\sigma}(\mathbf{r}_1)}. \end{aligned} \quad (10)$$

IV. SDFT ANALOG OF KOOPMANS' THEOREM

With the introduction of the response potential and the orbital expansions (6) and (8), we are able to achieve our purpose in this paper, namely to relate the energies $\epsilon_{i\sigma}$ of the KS spin-orbitals to observed quantities, namely, the vertical ionization potentials (VIPs) $I_i^{S'} = E_i^{(N-1)S'} - E_0^{NS}$. Inserting Eqs. (6) and (8) in the left-hand side of the first line of Eq. (10) and integrating both sides of this equality with the spin-orbital density $|\phi_{i\sigma}(\mathbf{r}_1)|^2$, we obtain the following linear equations for the orbital energies $\epsilon_{i\sigma}$:

$$\sum_j^{N_{\sigma}} M_{kj}^{\sigma} \epsilon_{j\sigma} = - \sum_{S'=(S-m_{\sigma})}^{S+1/2} \sum_{i[S'=(S-m_{\sigma})]} P_{ki}^{\sigma} I_i^{S'} + \epsilon_{k\sigma}^{\text{resp}}. \quad (11)$$

In Eq. (11) M_{kj}^{σ} and P_{ki}^{σ} are the integrals $M_{kj}^{\sigma} = \int |\phi_{k\sigma}(\mathbf{r}_1)|^2 |\phi_{j\sigma}(\mathbf{r}_1)|^2 / \rho_{\sigma}(\mathbf{r}_1) d\mathbf{r}_1$, $P_{ki}^{\sigma} = \int |\phi_{k\sigma}(\mathbf{r}_1)|^2 \times |d_{i\sigma}(\mathbf{r}_1)|^2 / \rho_{\sigma}(\mathbf{r}_1) d\mathbf{r}_1$ of the weighted overlap between the densities of the KS and Dyson orbitals. $\epsilon_{k\sigma}^{\text{resp}}$ is the orbital expectation value $\epsilon_{k\sigma}^{\text{resp}} = \int |\phi_{k\sigma}(\mathbf{r}_1)|^2 \nu_{\text{resp},\sigma}(\mathbf{r}_1) d\mathbf{r}_1$ of the response potential $\nu_{\text{resp},\sigma}$, which is defined independently in Eq. (10) through the functional derivatives. Note that, in order to derive Eq. (11) from Eqs. (6), (8), and (10), we have used our result [see discussion below Eq. (8)] that the energy of the highest occupied orbital of spin σ occurring in Eq. (8) is equal to minus the ionization energy $E_0^{(N-1)(\sigma)} - E_0^{NS}$ occurring in Eq. (6).

We will assume that in the infinite sum on the right-hand side of Eq. (11) the primary ionizations occur first. Primary ionizations are characterized by wave functions that can be reasonably well approximated by an orbital ionization, without further excitations. In case I, ionization out of the open shell leads to one primary ion state with spin $S-1/2$. Possible ion states with lower spin arising from this type of ionization have Dyson orbitals that are zero and do not play a role in the present context. Ionization from each fully occupied lower shell leads to two ion states with $S \pm 1/2$, with corresponding Dyson orbitals. There are fewer $S+1/2$ ion states, and fewer β Dyson orbitals (only associated with $S+1/2$ ion states), than $S-1/2$ ion states and α Dyson orbitals (associated with $S-1/2$ and $S+1/2$ ion states). Collecting the ionizations to $S+1/2$ and $S-1/2$ states in the vectors

$\mathbf{I}^{(S+1/2)}$ and $\mathbf{I}^{(S-1/2)}$, we obtain as formal solutions of Eq. (11) for α and β spins (ϵ_{σ} is the vector of one-electron energies of σ spin KS orbitals)

$$\epsilon_{\beta} = -\mathbf{M}_{\beta}^{-1} \mathbf{P}_{\beta}^{(S+1/2)} \mathbf{I}^{(S+1/2)} + \mathbf{M}_{\beta}^{-1} \epsilon_{\beta}^{\text{resp}}, \quad (12)$$

$$\begin{aligned} \epsilon_{\alpha} = & -\mathbf{M}_{\alpha}^{-1} \mathbf{P}_{\alpha}^{(S-1/2)} \mathbf{I}^{(S-1/2)} - \mathbf{M}_{\alpha}^{-1} \mathbf{P}_{\alpha}^{(S+1/2)} \mathbf{I}^{(S+1/2)} \\ & + \mathbf{M}_{\alpha}^{-1} \epsilon_{\alpha}^{\text{resp}}. \end{aligned} \quad (13)$$

With Eqs. (12) and (13), the energies of the KS spin-orbitals of a particular spin σ are related to energies of ionization to $(N-1)$ electron states of spins $(S+1/2)$ and $(S-1/2)$. Only VIPs to higher-spin $(S+1/2)$ states determine minor spin (β) orbital energies, while VIPs to both $(S+1/2)$ and $(S-1/2)$ states determine major spin (α) orbital energies.

It is anticipated (Ref. 11, see also Refs. 18 and 19) that for a particular KS orbital $\phi_{i\sigma}$ the largest elements $w_{ij}^{S',\sigma} = (\mathbf{M}_{\sigma}^{-1} \mathbf{P}_{\sigma}^{S'})_{ij}$ in Eqs. (12) and (13) are with Dyson orbitals of the corresponding primary ionizations, ϕ_i^{-1} , i.e., $d_{\beta}^{S+1/2,S+1/2}(\phi_i^{-1})$ in Eq. (12) and $d_{\alpha}^{S+1/2,S-1/2}(\phi_i^{-1})$ and $d_{\alpha}^{S-1/2,S-1/2}(\phi_i^{-1})$ in Eq. (13) (we label the Dyson orbitals with the S, M quantum numbers and the orbital configuration of the corresponding ion state). Considering first the β spin orbital energies, this leads to identification of the energies $\epsilon_{i\beta}$ in Eq. (12) with ionization energies to the primary $(S+1/2)$ states, $\epsilon_{i\beta} \approx -I^{(S+1/2)}(\phi_i^{-1})$, with corrections coming from the coupling to other $(S+1/2)$ states and from the response matrix elements. The latter are quite small for valence levels, cf. Ref. 11. Since surely the highest β orbital energy, which we list as the first one in the ϵ_{β} vector, is exactly equal to the lowest ionization energy to an $(S+1/2)$ state, $-I^{S+1/2}(\phi_H^{-1})$, the element $w_{11}^{(S+1/2),\beta}$ is expected to be close to 1, and all other terms in the total sum that makes up $\epsilon_{H\beta}$ to almost cancel.

Turning next to the open-shell orbitals, in case I the energies of $(N_{\alpha} - N_{\beta})$ open shell α orbitals, which have all α spin occupation in this case, are identified from Eq. (13) with the ionization energies to the corresponding primary $(S-1/2)$ states, $\epsilon_{H\alpha} \approx -I_h^{S-1/2}(\phi_H^{-1})$ (ϕ_H^{-1} denotes the configuration resulting from ionization out of the open shell, and ϕ_h is one of the KS orbitals belonging to the open shell). For the highest occupied orbital we certainly have the exact identity $\epsilon_{H\alpha} = -I^{S-1/2}(\phi_H^{-1})$. We expect for the other open shell orbitals ϕ_h close proximity of the orbital energies to $-I^{S-1/2}(\phi_H^{-1})$, but whether these will be exactly identical to $-I^{S-1/2}(\phi_H^{-1})$ or not depends on the spatial symmetry properties of the Kohn–Sham model, an as yet unsolved problem. In case II, as follows from the previous discussion, the highest α and β orbitals, belonging both to the open shell, are degenerate, which yields $\epsilon_{H\alpha} = \epsilon_{H\beta} = -I^{S+1/2}(\phi_H^{-1})$.

Considering finally the other α orbitals, belonging to the closed shells, we note that in both cases I and II $(S+1/2)$ as well as $(S-1/2)$ states corresponding to the primary ionization ϕ_i^{-1} contribute to Eq. (13), so that the orbital energy is a weighted sum of the corresponding VIPs, $\epsilon_{i\alpha} \approx -w_{ii}^{(S+1/2),\alpha} I^{(S+1/2)}(\phi_i^{-1}) - w_{ii}^{(S-1/2),\alpha} I^{(S-1/2)}(\phi_i^{-1})$ (with corrections from other primary ionizations). The $(S+1/2)$

states are presumably lower in energy than the $(S-1/2)$ ones. Compared to the β spin orbital energies, the α (majority) spin orbital energies will have admixture of the (negative of the) ionization energy to the higher $(S-1/2)$ states, which would imply that (provided that the weights $w_{ii}^{S',\sigma}$ sum approximately to 1) the corresponding major spin α KS orbital energy of this shell will be more negative than the corresponding minor spin orbital energy $\epsilon_{i\beta} \approx -I^{(S+1/2)}(\phi_i^{-1})$. This explains a well-known characteristic feature of SDFT.

Consider, as a simple special case, a doublet ground state $\Psi_{N,1/2,1/2}^{N,1/2,1/2}$ with one α electron outside closed shells (case I). The cationic ground state is the singlet $\Psi_0^{(N-1),0,0}(\phi_H^{-1})$, where the configuration corresponding to removal of the electron from the highest (singly) occupied orbital is denoted (ϕ_H^{-1}) . The energy of the highest α orbital is equal to the energy of ionization to this state, $\epsilon_{H\alpha} = -I^0(\phi_H^{-1})$. The lower lying doubly occupied orbitals have KS β orbital energies $\epsilon_{i\beta}$ approximately equal to ionization energies to the primary triplet states $\Psi_i^{(N-1),1,M}(\phi_i^{-1})$, $\epsilon_{i\beta} \approx -I^1(\phi_i^{-1})$, and for the highest β orbital $\epsilon_{(H-1)\beta} = -I^1(\phi_{H-1}^{-1})$. The energies $\epsilon_{i\alpha}$ of the closed-shell α orbitals will be weighted sums $\epsilon_{i\alpha} \approx w_{ii}^{1,\alpha} I^1(\phi_i^{-1}) + w_{ii}^{0,\alpha} I^0(\phi_i^{-1})$ of the energies of ionization to the states $\Psi_i^{(N-1),1,M}(\phi_i^{-1})$ and $\Psi_i^{(N-1),0,M}(\phi_i^{-1})$ produced by the triplet and singlet spin-coupling of the unpaired electron in the outer shell to the unpaired electron in the ionized shell.

To estimate the weights of $I^1(\phi_i^{-1})$ and $I^0(\phi_i^{-1})$, let us consider as example the doublet ground state of Li atom approximated with a single spin-restricted determinant, $\Psi^{3,1/2,1/2} \approx |1s(\mathbf{r}_i)\alpha(s_i)1s(\mathbf{r}_j)\beta(s_j)2s(\mathbf{r}_k)\alpha(s_k)|$. Then, the singlet cationic ground state is in the frozen orbital (Koopmans') approximation $\Psi_0^{2,0,0}(2s^{-1}) \approx |1s(\mathbf{r}_i)\alpha(s_i) \times 1s(\mathbf{r}_j)\beta(s_j)|$. The "overlap" of $\Psi_0^{2,0,0}(2s^{-1})$ with $\Psi^{3,1/2,1/2}$ yields the Dyson α -orbital $d_{\alpha}^{0,0}(\phi_H^{-1}) = (2s)$. The matrix elements $M_{\alpha 11}$ and $P_{\alpha 11}^{(S-1/2)}$ are equal in the current approximation and one obtains straightforwardly from Eq. (13) that the first element of the ϵ_{α} vector becomes $-I^0(2s^{-1})$ (approximately with our approximations; exactly if the wave functions would be exact).

Ionization out of the $1s$ shell produces triplet and singlet cationic states. The $M=0$ singlet $\Psi^{2,0,0}(1s^{-1}) \approx (1/\sqrt{2}) \times (|1s(\mathbf{r}_1)\alpha(s_1)2s(\mathbf{r}_2)\beta(s_2)| - |1s(\mathbf{r}_1)\beta(s_1)2s(\mathbf{r}_2)\alpha(s_2)|)$ and the triplet $\Psi^{2,1,0}(1s^{-1}) \approx (1/\sqrt{2}) \times (|1s(\mathbf{r}_1)\alpha(s_1) \times 2s(\mathbf{r}_2)\beta(s_2)| + |1s(\mathbf{r}_1)\beta(s_1)2s(\mathbf{r}_2)\alpha(s_2)|)$ states yield two identical Dyson α -orbitals (the sign is arbitrary) $d_{\alpha}^{0,0}(1s^{-1}) = d_{\alpha}^{1,0}(1s^{-1}) = (1/\sqrt{2})(1s)$. The structure of the \mathbf{M}_{α} and $\mathbf{P}_{\alpha}^{(S-1/2)}$ and $\mathbf{P}_{\alpha}^{(S+1/2)}$ very much simplifies in this case, and it is easy to see that the factor $1/\sqrt{2}$ in front of the $1s$ both in the "singlet Dyson orbital" $d_{\alpha}^{0,0}(1s^{-1})$, which enters $\mathbf{P}_{\alpha}^{(S-1/2)}$ and determines the contribution of $I^0(1s^{-1})$, and in the "triplet Dyson orbital" $d_{\alpha}^{1,0}(1s^{-1})$, which enters $\mathbf{P}_{\alpha}^{(S+1/2)}$ and determines the contribution of $I^1(1s^{-1})$, has the effect that the energy $\epsilon_{1s\alpha}$ of the KS closed-shell α orbital is (approximately) a fifty-fifty mixture of the ionization energies to the $\Psi^{2,0,0}(1s^{-1})$ and $\Psi^{2,1,0}(1s^{-1})$ states, $\epsilon_{1s\alpha} \approx -\frac{1}{2}(I^1(1s^{-1}) + I^0(1s^{-1}))$. With this example in mind, one can infer in the general case of one α electron outside closed shells, that the energies of the closed-shell α

orbitals represent approximately an equal mixture of singlet and triplet ionization energies, $\epsilon_{i\alpha} \approx -\frac{1}{2}(I^1(\phi_i^{-1}) + I^0(\phi_i^{-1}))$. In the general case of an open shell ground state with spin S , it is a simple matter to deduce from elementary spin coupling rules that the Dyson orbitals corresponding to the ion states $\Psi^{(N-1)(S+1/2,S-1/2)}(\phi_i^{-1})$ and $\Psi^{(N-1)(S-1/2,S-1/2)}(\phi_i^{-1})$, which give rise to α -spin Dyson orbitals, are in the Koopmans' frozen orbital approximation $d_{\alpha}^{S+1/2,S-1/2}(\mathbf{r})\alpha(s) = (1/\sqrt{2S+1})\phi_i(\mathbf{r})\alpha(s)$ and $d_{\alpha}^{S-1/2,S-1/2}(\mathbf{r})\alpha(s) = \sqrt{2S/2S+1}\phi_i(\mathbf{r})\alpha(s)$, respectively. This leads to the approximate

$$\epsilon_{i\alpha} \approx -\left(\frac{2S}{2S+1}I^{S-1/2}(\phi_i^{-1}) + \frac{1}{2S+1}I^{S+1/2}(\phi_i^{-1})\right).$$

V. CONCLUSIONS

In this paper, starting from the ground-state Schrödinger equation for the wave function with the spin S , the analysis and interpretation of spin-density functional theory has been presented. It has been shown that with the physically reasonable zero gauges, the spin-unrestricted xc potential of the equation for $\sqrt{\rho_{\sigma}}$ and the spin-unrestricted KS xc potential $\nu_{xc\sigma}$ can be represented in a physically meaningful way [Eqs. (4) and (9)] as the potential of the xc-hole $\nu_{xc,\sigma}^{\text{hole}}$ surrounding an electron with the spin σ plus corrections defined in terms of the spin-resolved conditional probability amplitudes Φ_{σ} and $\Phi_{s\sigma}$. Thus, in the considered case of the two-component KS potentials (magnetic interactions are neglected) the proper fixing of the nonuniqueness of $\nu_{xc\sigma}$ pointed out in Ref. 7 allows an interpretation of $\nu_{xc\sigma}$ similar to that given for the spin-restricted KS DFT of closed-shell systems in Refs. 9, 10, and 12.

Exact relations (12) and (13) between the KS orbital energies $\epsilon_{i\sigma}$ and energies $-I^{S'}(\phi_i^{-1})$ of ionization to the states of a certain spin S' have been derived. Their approximate interpretation provides the KS SDFT analog of the celebrated Koopmans' theorem.⁸ In particular, the minor spin orbital energies $\epsilon_{i\beta}$ are approximately identified in all cases with primary ionizations to the states of the higher spin $(S+1/2)$,

$$\epsilon_{i\beta} \approx -I^{S+1/2}(\phi_i^{-1}) \quad (14)$$

(exact identity for $\epsilon_{H\beta}$). The energies $\epsilon_{i\alpha}$ of the major spin orbitals of closed shells ($1 \leq i \leq N_{\beta}$) in all cases and those of the open shell (except $\epsilon_{H\alpha}$) in case II are represented with the weighted sum of higher- and lower-spin VIPs,

$$\epsilon_{i\alpha} \approx -\left(\frac{2S}{2S+1}I^{S-1/2}(\phi_i^{-1}) + \frac{1}{2S+1}I^{S+1/2}(\phi_i^{-1})\right). \quad (15)$$

In case I the energies $\epsilon_{i\alpha}$ of the open-shell orbitals are represented with the lower-spin VIPs,

$$\epsilon_{i\alpha} \approx -I^{S-1/2}(\phi_i^{-1}) \quad (\text{case I}) \quad (16)$$

(exact identity for $\epsilon_{H\alpha}$) and in case II the highest occupied α and β orbitals of the open shell are degenerate

$$\epsilon_{i\alpha} = \epsilon_{i\beta} = -I^{S+1/2}(\phi_i^{-1}) \quad (\text{case II}). \quad (17)$$

Comparison of Eqs. (14) and (15) provides an explanation for a characteristic feature of SDFT, the lower major-spin orbital energies of closed shells compared to the corresponding minor-spin ones, $\epsilon_{i\alpha} < \epsilon_{i\beta}$. However, none of the standard SDFT approximations can provide the degeneracy (17), which follow from the asymptotic conditions satisfied with the zero gauge as have been discussed in Secs. II and III. Then, an adequate model for the potential $v_{xc\alpha}$ should exhibit a positive build-up in the region of the highest α -orbital $\phi_{H\alpha}$, which would provide the required degeneracy (17) and, at the same time, would not prevent the relative stabilization (15) of other α -orbitals. In general, the present SDFT relations (14)–(17) of the Koopmans' type can be used to calibrate approximate spin-unrestricted KS SDFT xc potentials from the reliable data (VIPs) of photoelectron spectroscopy.

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